

## The Electrochemical Deposition and Properties of $H_I$ -e Nanostructured Films of Palladium

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Over the last four years a novel method for the electrodeposition of nanostructured metal films has been developed in Southampton. This method uses lyotropic liquid crystalline phases as templates for the desired nanostructure [1-3] and exploits the ability of mixtures of surfactant molecules and aqueous solutions to spontaneously assemble into regular structures with nanometre dimensions. The resulting nanostructured metal films are characterized by high specific surface areas (greater than  $10^6 \text{ cm}^2/\text{cm}^3$ ), uniform pore size distribution and long range order. These properties, together with the good mechanical stability of the films, favour the application of these nanostructured materials in batteries, fuel cells, sensors etc.

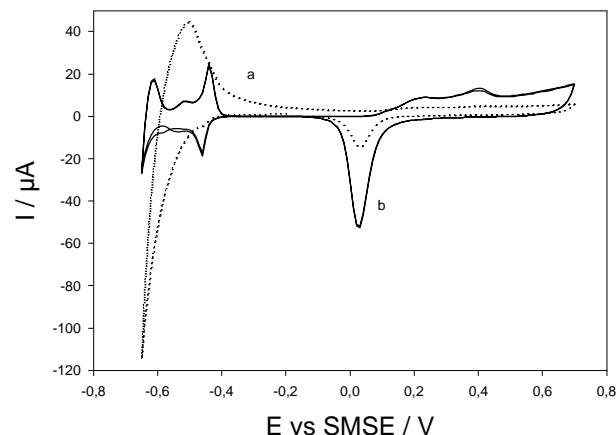
In the present work we have investigated the preparation and properties on nanostructured films of palladium deposited from the hexagonal ( $H_I$ ) lyotropic phase. These  $H_I$ -e palladium films are typically 0.1 to 0.5 microns thick and punctured by a regular hexagonal array of continuous cylindrical pores around 2.5 nm in diameter and with a center to center spacing of around 5.5 nm. This gives a film with a very high surface area and one in which the thickness of the palladium walls between the pores is never more than about 3 nm.

The electrochemical deposition of the  $H_I$ -e nanostructured palladium films was carried out from the hexagonal phase formed by a mixture of a non-ionic surfactant,  $C_{16}EO_8$  or Brij® 56, and an aqueous solution of  $(\text{NH}_4)_2\text{PdCl}_4$ . The phase behavior of the system was established using polarizing light microscopy and the conditions for electrochemical deposition were selected to ensure that the system was in the hexagonal ( $H_I$ ) phase. The structure and morphology of the electrodeposited films was established by transmission electron microscopy (TEM), low angle X-ray diffraction (XRD) and scanning electron microscopy (SEM).

It is well known that palladium can absorb large quantities of hydrogen [4] and that surface modification of palladium electrodes can be used to discriminate between adsorbed and absorbed hydrogen [5]. Cyclic voltammetric studies of the  $H_I$ -e nanostructured palladium films were carried out in acid solution. These experiments show that the nanostructure is stable towards repeated cycling and possess unique properties by virtue of its high surface area and nanostructure.

Figure 1 shows a comparison of the voltammetry for an  $H_I$ -e palladium film and a polycrystalline palladium wire recorded in  $1 \text{ mol dm}^{-3}$  sulfuric acid. In the case of the polycrystalline wire (figure 1 a) there are no well resolved hydrogen adsorption or absorption peaks, rather the voltammetry shows broad featureless reduction or oxidation at negative potentials. In contrast for the  $H_I$ -e nanostructured palladium film (figure 1 b) the voltammetry shows well defined peaks corresponding to hydrogen adsorption and absorption. In this respect the voltammetry of these nanostructured films is similar to that reported for nanoparticles of palladium supported on

carbon electrode surfaces [5] or for very thin layers of palladium deposited onto single crystal platinum electrode surfaces [4] where the distance over which hydrogen atoms can diffuse into the palladium is also restricted to 2 nm or less.



**Figure 1:** Cyclic voltammograms for a) a polycrystalline Pd wire and b)  $H_I$ -e nanostructured Pd film deposited on a gold disc electrode (1mm diameter) recorded in  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at  $20 \text{ mV s}^{-1}$ .

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